

Hf defects in HfO₂/Si

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We investigate the possibility that Hf defects exist in the Si channel of HfO₂/Si-based metal-oxide-semiconductor devices. We have studied, using *ab initio* Density Functional Theory calculations, substitutional and interstitial Hf impurities in *c*-Si, for various charge states. Our results indicate that 1) the tetrahedral interstitial defect is energetically more favorable than the substitutional, and 2) there are various stable charge states in the Si gap. The possible presence of these charged impurities in the Si channel could lead to a mobility reduction, due to coulombic scattering.

The continued scaling down of silicon-based complementary metal-oxide-semiconductor (CMOS) technology has required intense search for high-*k* gate dielectric materials that can replace SiO₂. In particular, HfO₂ has been considered as one of the most promising candidates, due to its large band gap, high dielectric constant, low leakage current, and its thermodynamic stability on Si [1, 2]. However, for the successful integration of this high-*k* material with the Si/CMOS technology there are still a number of fundamental issues that must be solved, such as reduced channel mobility and charge trapping states at the oxide.

Previous works[3, 4] have reported that the channel mobilities in CMOS devices with HfO₂ gate dielectrics are significantly degraded when compared to SiO₂. A possible mechanism to explain this behavior is the remote Coulomb scattering (RCS) due to charge trapping centers at the Si/HfO₂ interface. We here investigate, using state-of-the-art first principles calculations, possible additional charge trapping centers related to Hf impurity defects in Si. Even though under equilibrium conditions Hf atoms do not have a significant solubility in Si, non-equilibrium growth conditions where the HfO₂ is grown directly on top of the Si substrate may lead to the incorporation of a small number of Hf atoms as impurities, in a narrow region close to the Si/HfO₂ interface [5, 6].

In this work, we have investigated the formation energy of different Hf impurity defects in *c*-Si, through first-principles calculations, based on the Density Functional Theory (DFT). In particular, we study Hf at substitutional (Hf_{Si}) and interstitial sites. For interstitial Hf defects, we have studied two different configurations: (i) Hf at tetrahedral sites (Hf_T^T); and (ii) Hf at hexagonal sites (Hf_H^H). For all cases studied we considered various charges states *q*. The main conclusion is that there are many charge states in the Si gap associated with these defects, which may lead also to detrimental coulombic scattering.

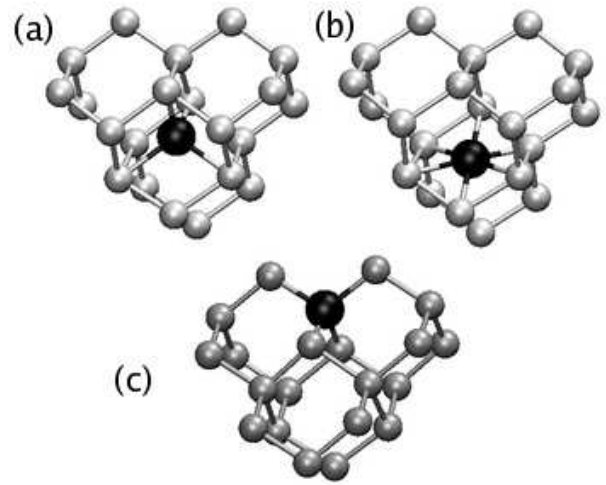


FIG. 1: Schematic geometries of defects in *c*-Si. Atomic structure of (a) a tetrahedral interstitial, (b) a hexagonal site, and (c) a substitutional defect. The black spheres (larger) represent Hf atoms, and the gray spheres (smaller) represent Si atoms.

The DFT calculations were performed using ultra-soft Vanderbilt pseudopotentials [11], and the generalized gradient approximation (GGA) for the exchange-correlation potential as implemented in VASP code [7, 8, 9, 12]. In order to study the interstitial and substitutional defects in Si, we have used 129 atoms (128 Si atoms and 1 Hf atom) and 128 atoms (127 Si atoms and 1 Hf atom) supercells, respectively. We have used a plane-wave-cutoff energy of 151 eV and the Brillouin zone was sampled at the *L*-points. In all calculations the atoms were allowed to relax until the atomic forces were smaller than 0.025 eV/Å. Spin polarized calculations were also performed, but we observed that the effect were very small regarding the total energies. Thus, we will report below only the non-spin polarized results.

The final relaxed geometries for the neutral defects are presented in Fig. 1. In Fig. 1(a) we show the tetrahedral interstitial defect. The Hf has four Si nearest neighbors

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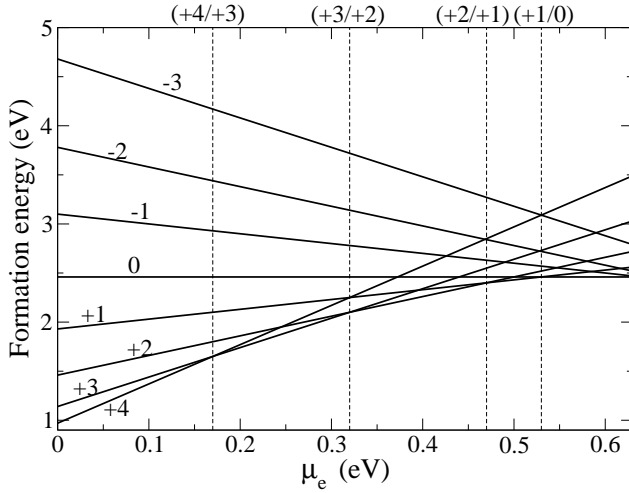


FIG. 2: Formation energy as function of the Fermi level μ_e for Hf defects at tetrahedral interstitial sites in *c*-Si, for a hafnium-rich growth condition. The numbers on the lines indicate defects charge states.

with Hf-Si bonds of approximately 2.50 Å. In Fig. 1(b) the Hf_I^H defect is presented. The Hf atom has now six Si nearest neighbors with average Hf-Si bond lengths of 2.54 Å. Finally, in Fig. 1(c) the Hf_{Si} is shown, and as can be seen the Hf atom has also four Si nearest neighbors with Hf-Si bond lengths of approximately 2.57 Å. Therefore, there is a global outward relaxation of about 14% for the Hf-Si bonds when compared to the original Si-Si bonds, which is caused by the larger Hf atomic radius. We have also investigated the possible existence of a dumbbell structure for the interstitial defect, since this is the lowest energy configuration for the Si self-interstitial. However, this structure turned out to be unstable, relaxing towards the tetrahedral defect. This is most likely caused by the larger Hf radius. For all the different charge states the final geometries were only slightly modified, with variations in the Hf-Si bonds of less than 0.05 Å. Small Jahn-Tell distortions were also observed in some cases. However, none of these effects alter in any qualitative way our main conclusion, which is the existence of charge states in the gap. Therefore, we will not analyze them in any further detail below.

The formation energy for a substitutional defect in the charge state q is calculated as

$$E_f^q(\text{Hf}_{Si}) = E_t^q(\text{Hf}_{Si}) - \frac{N_{Si}}{N} E_t(c\text{-Si}) - \mu_{Hf} + q(\mu_e + E_v), \quad (1)$$

whereas for the interstitial defects in the charge state q it is calculated as

$$E_f^q(\text{Hf}_I) = E_t^q(\text{Hf}_I) - E_t(c\text{-Si}) - \mu_{Hf} + q(\mu_e + E_v) \quad (2)$$

In the above expressions, $E_t^q(D)$ are the total energies of the fully relaxed supercells with the substitutional or

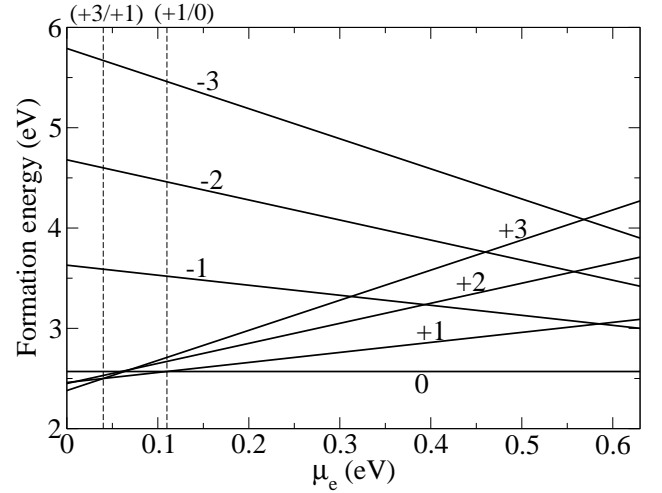


FIG. 3: Formation energy as function of the Fermi level μ_e for Hf defects at substitutional interstitial sites in *c*-Si for a Hf-rich growth condition. The numbers on the lines indicate defects charge states.

interstitial defect D , and $E_t(c\text{-Si})$ is the total energy of the similar supercell for the perfect crystal of *c*-Si; μ_e is electronic chemical potential, N_{Si} is the number of Si atoms and N is the total number of atoms in the supercell. We have considered the bulk *c*-Si as the source of Si atoms. The value for the Hf chemical potential, μ_{Hf} , depends on the growth conditions. We will consider the limits of Hf-rich conditions and O-rich conditions similarly to our previous work [10].

For the neutral interstitials, we obtain that the formation energy for the Hf_I^H is 2.3 eV larger than for the Hf_I^T . Therefore, we will only analyse in detail below the Hf_I^T defect. In Fig. 2 we present the formation energies for the Hf_I^T defect in different charge states q , calculated via Eq. 2. The formation energies are plotted as a function of μ_e , which is varied between the theoretical values of the valence band maximum ($\mu_e = 0$ eV) and conduction band minimum ($\mu_e = 0.63$ eV). The values reported in Fig. 2 are for Hf-rich conditions [10]. For oxygen rich conditions the curves would have to be up shifted by 10.9 eV. We have studied charge states with q varying from (+4) to (-3). As can be seen, there are many equilibrium charge states in the gap, five total, from (+4) to (0). This gives rise to four transition levels, the (+4/+3), (+3/+2), (+2/+1), and (+1/0) at μ_e equal to 0.17 eV, 0.32 eV, 0.47 eV, and 0.53 eV, respectively. This indicates that for a large range of electronic chemical potentials there will be charged states that can contribute to coulombic scattering at the channel. It is important to stress that the particular value of the transition level may change due to the well known limitation of DFT in describing the band gap (our theoretical band gap is 0.63 eV whereas the experimental gap is 1.17 eV). However, the important point of our paper, which is the existence of these charged states, does not depend on these possible

shifts of the transition levels.

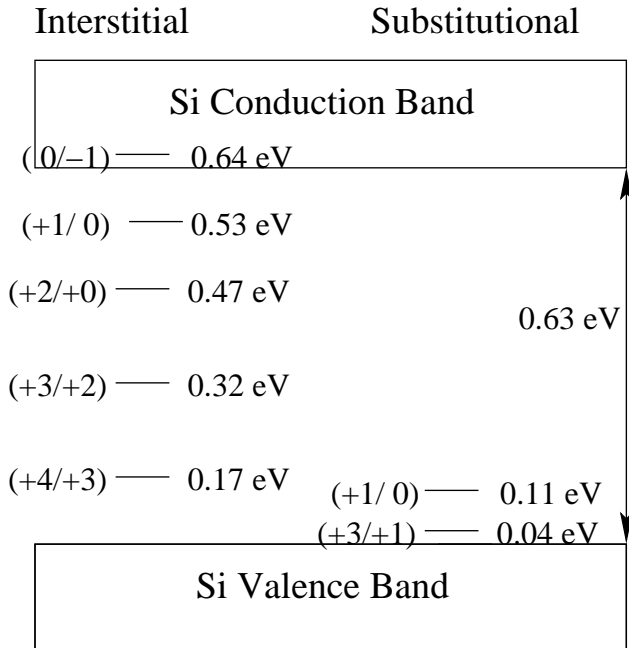


FIG. 4: Schematic structure for the transition levels in the gap, for the Hf_I^T impurity defect (left) and the Hf_{Si} defect (right). We use the theoretical band gap of 0.63 eV.

The formation energies for substitutional Hf defects, calculated according to Eq. 1, are presented in Fig. 3. The choices of chemical potentials are the same as in Fig. 2. As can be seen, the neutral defect is stable for a large range of the electronic chemical potential. This is expected due to the "isovalent character" of Hf when

compared to Si. However, for μ_e close to the top of the valence band there are two transition levels. Very close to the top of the valence band the (+3) charge state is stable, with the (+3/+1) transition level at $\mu_e = 0.04$ eV, having, thus, a small negative-U character. The second (+1/0) transition level is at $\mu_e = 0.11$ eV.

Comparing the interstitial and substitutional defects, we see that the Hf_I^T is more stable than the Hf_{Si} in the entire range of the electronic chemical potential. For p-type materials the Hf_I^T is almost 1.5 eV more stable than the Hf_{Si} , whereas for n-type materials this same difference is only of the order of 0.1 eV.

In summary, as shown in Fig. 4, we have shown that Hf impurity defects in Si will lead to many stable charged states in the gap, resulting in detrimental coulombic scattering and reducing the mobility in the channel. For p-type Si, the interstitial Hf impurities will be in a (+4) charge state, and they are more stable than the substitutional sites by more than 1.25 eV. However, if only substitutional impurities were present due to the growth conditions, they would also be charged. For n-type material the neutral substitutional defect is now more stable, but with formation energies very close to ones for the interstitial defect. In any case, it seems that Hf may be more detrimental in p-type Si. Finally, it would be very important if experimental works could investigate the possible presence of these impurities.

Acknowledgments

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